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(54) Four-component glass for optical fibres

(57) Alkali metal borosilicate glass compositions modified by alkaline earth metal oxides are especially suitable for the production of graded index optical fibre by thermal diffusion using the double crucible method. The composition of the glass is calculated by taking a sodium borosilicate composition in region A of Fig. 1 of the drawings and replacing sodium oxide or sodium oxide and silica by alkaline earth metal oxide.

Using these glasses, fibres have been produced having refractive index profiles that approximate closely to the ideal parabolic distribution, numerical apertures of up to 0.21, and best loss values as low as 6.4dB/km at 850nm.

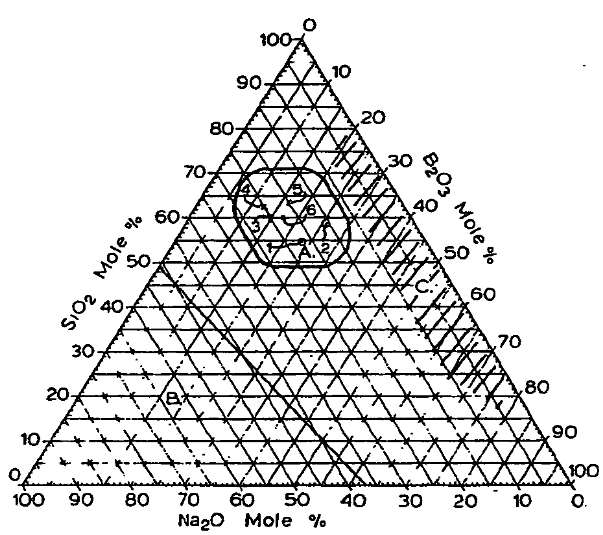

Fig. 1

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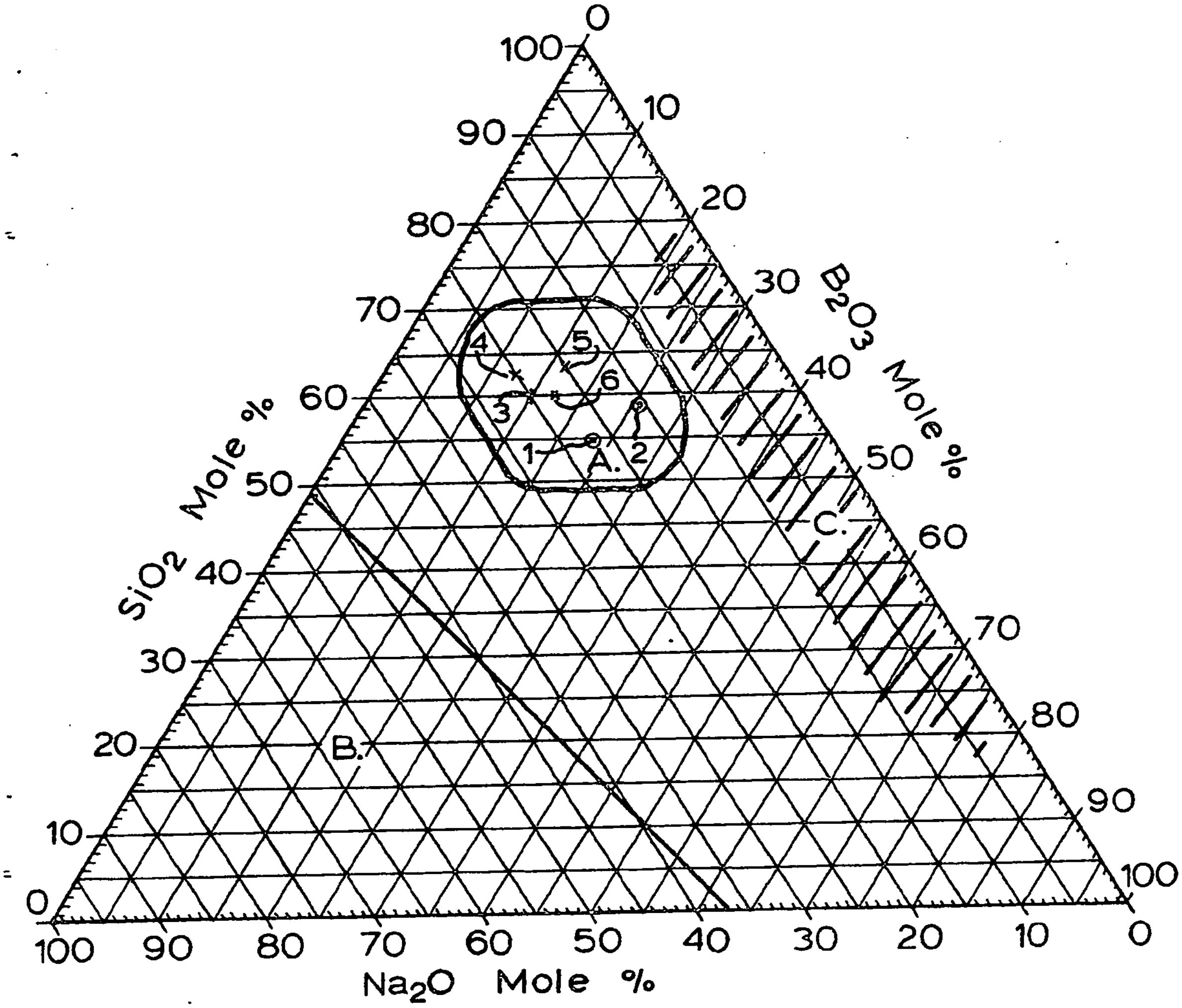

Fig.1

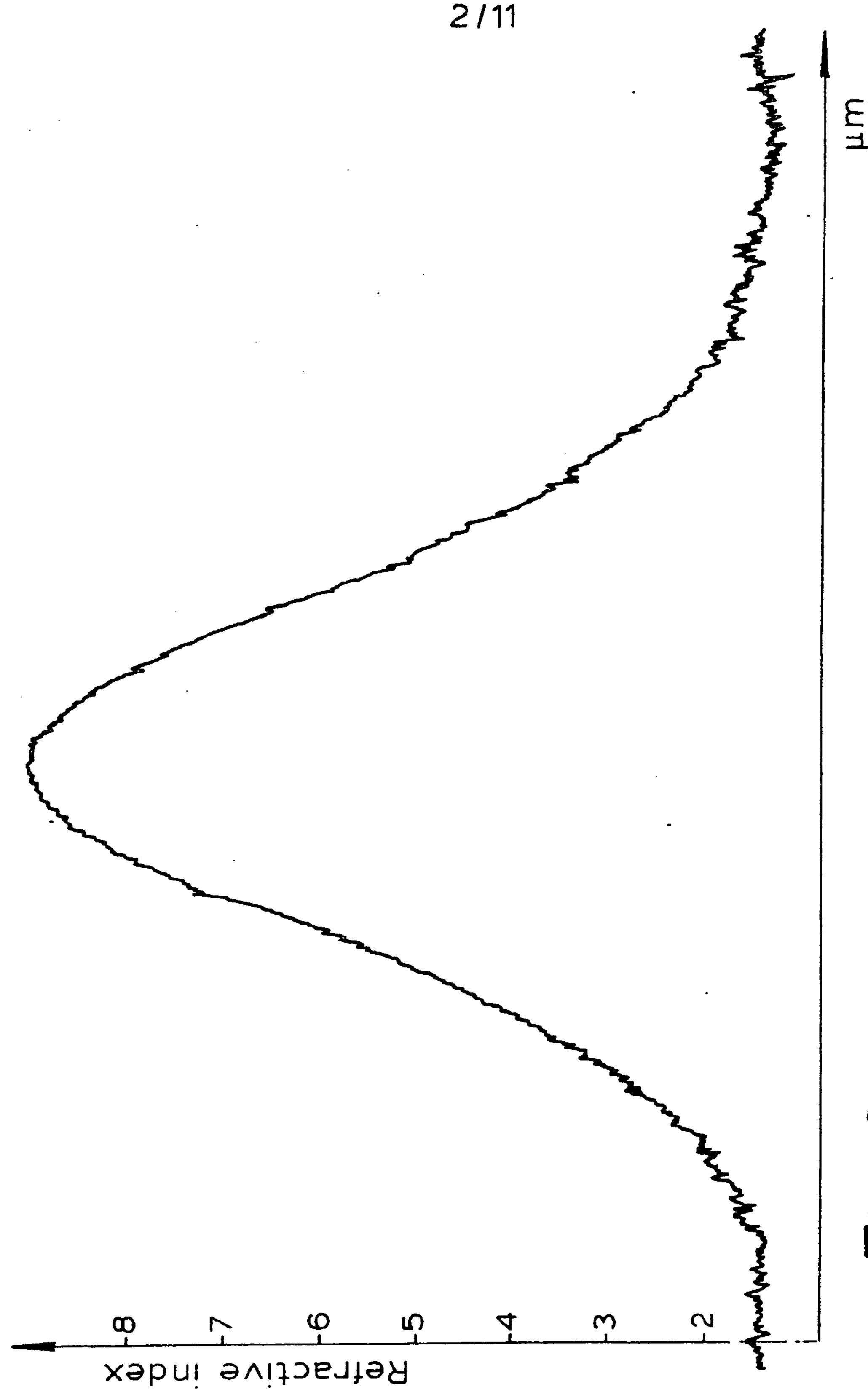

Fig. 2

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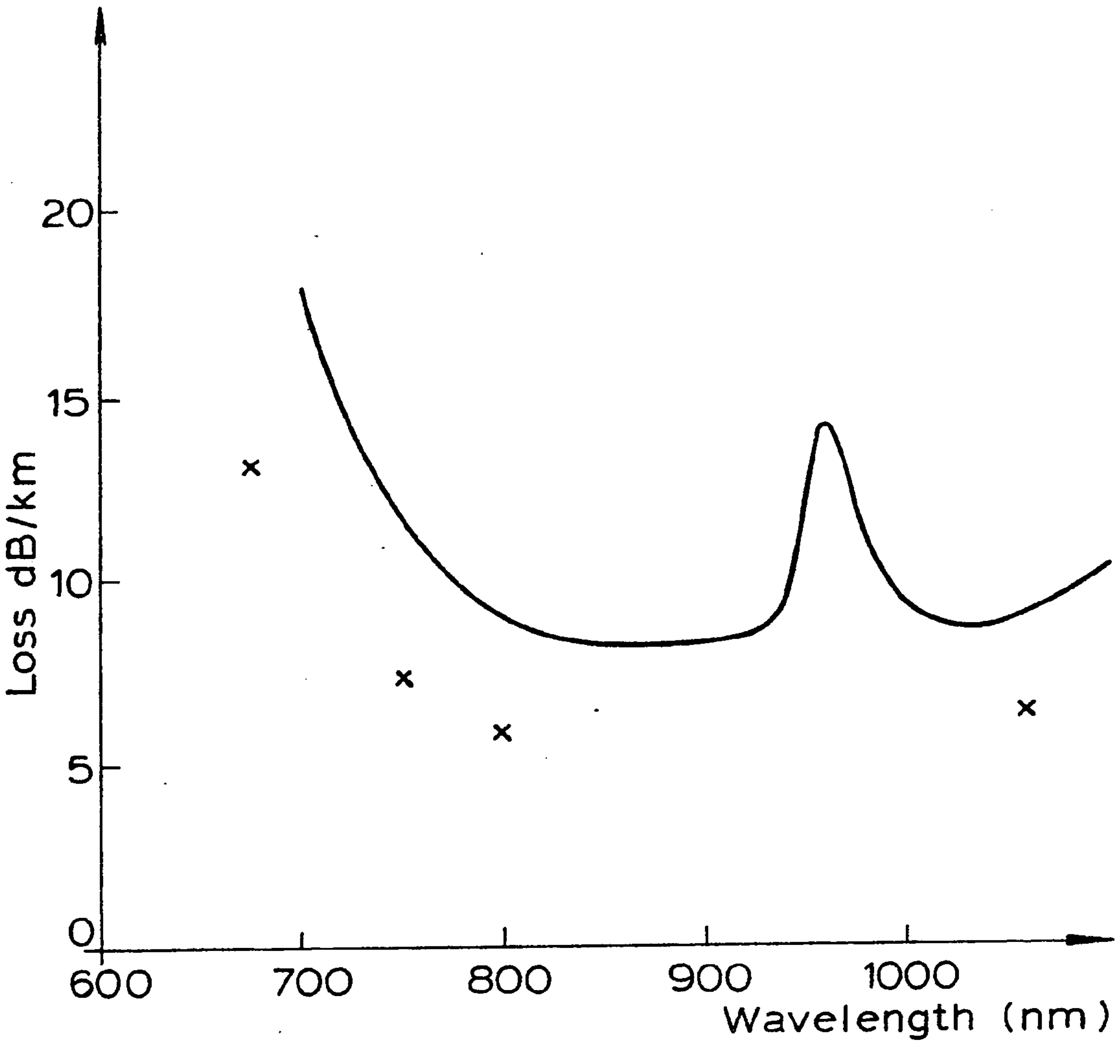

Fig.3

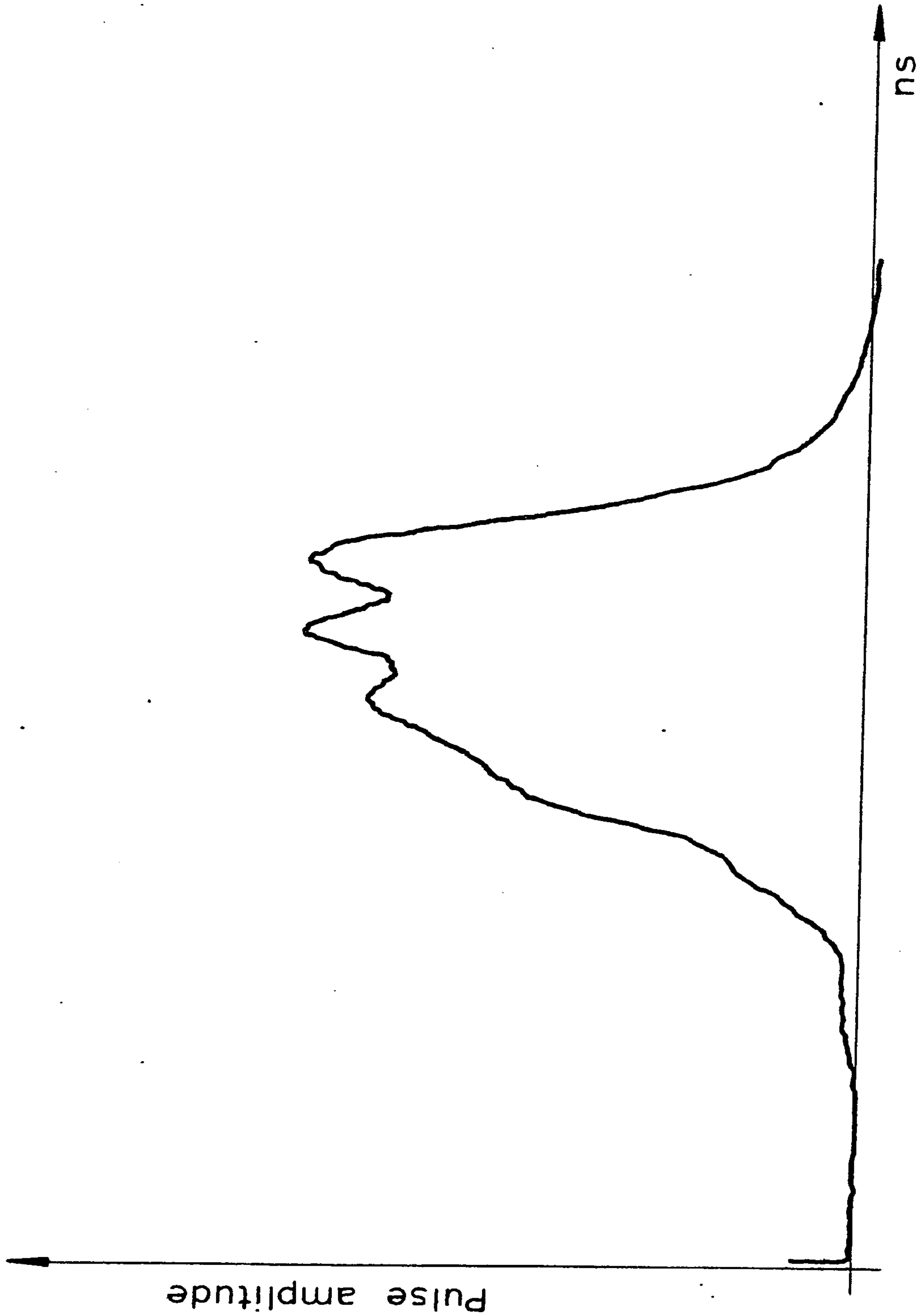

Fig.4

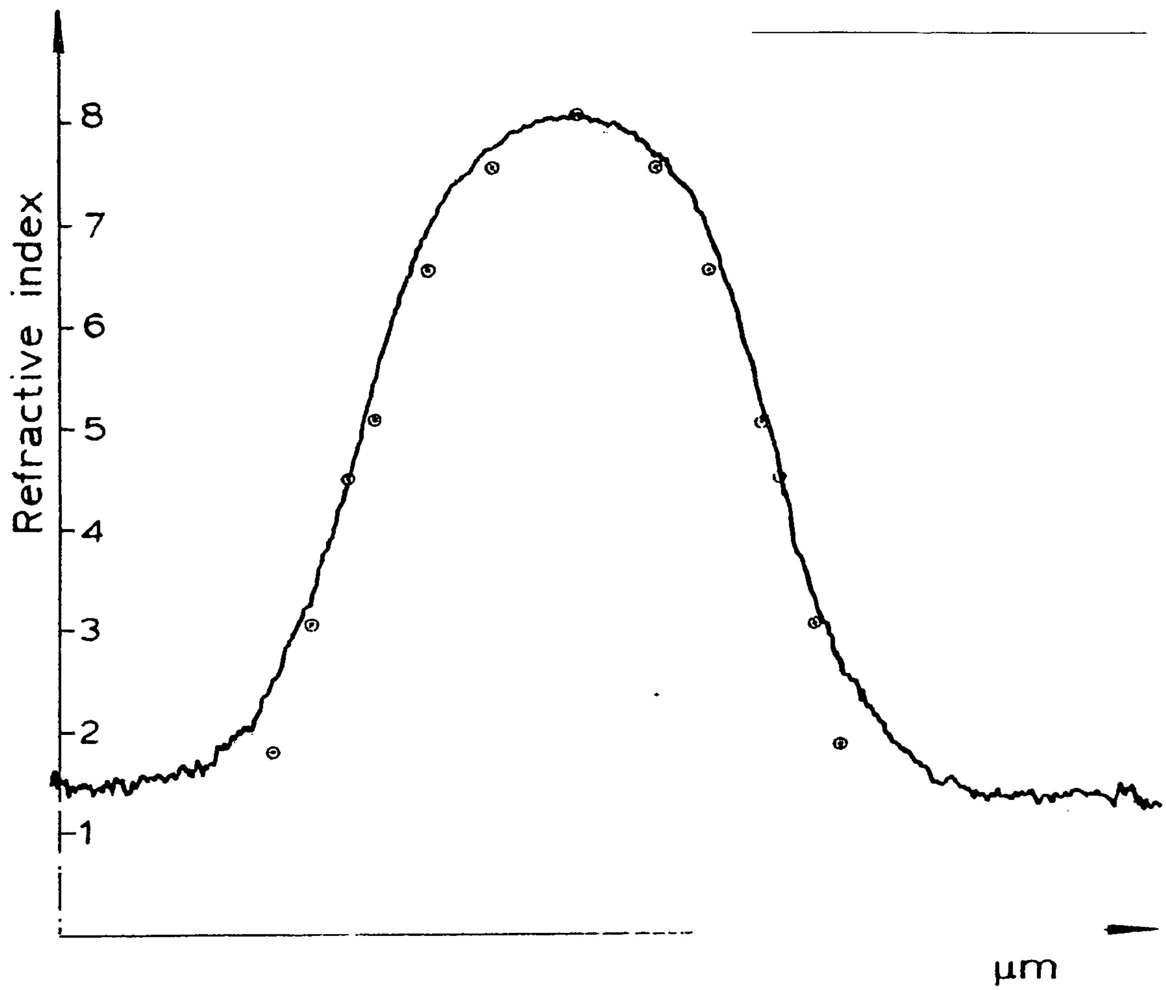

Fig. 5

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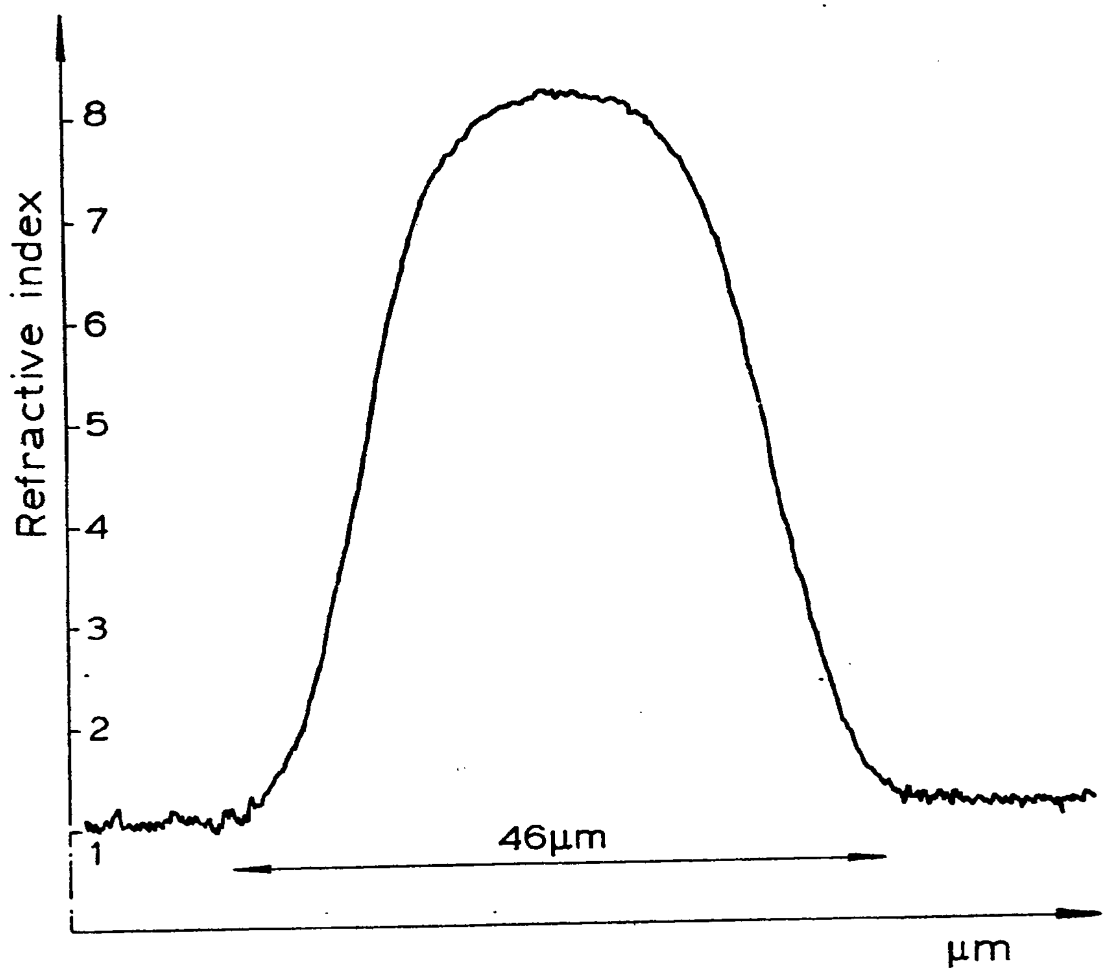

Fig. 6

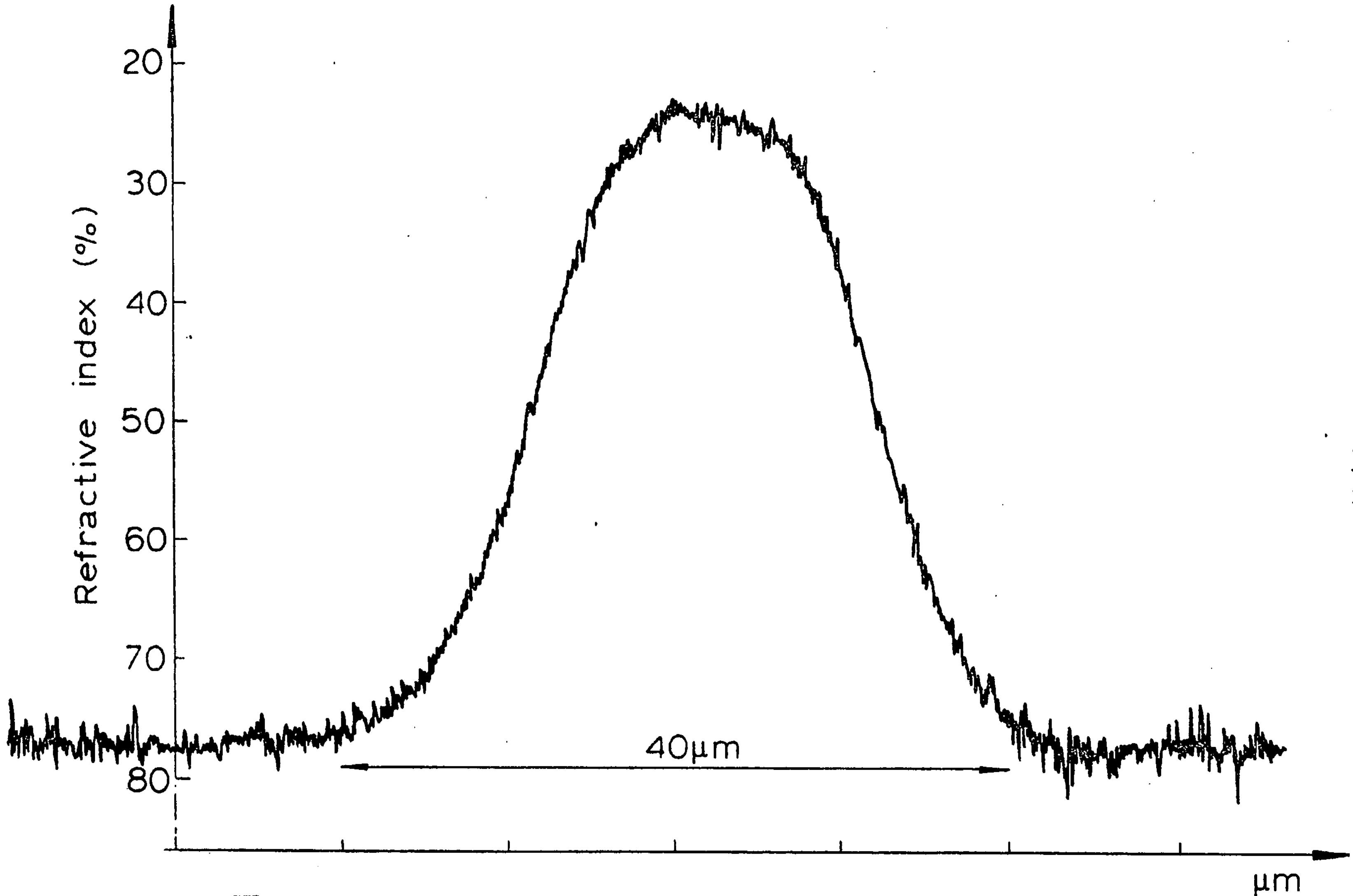

Fig. 7

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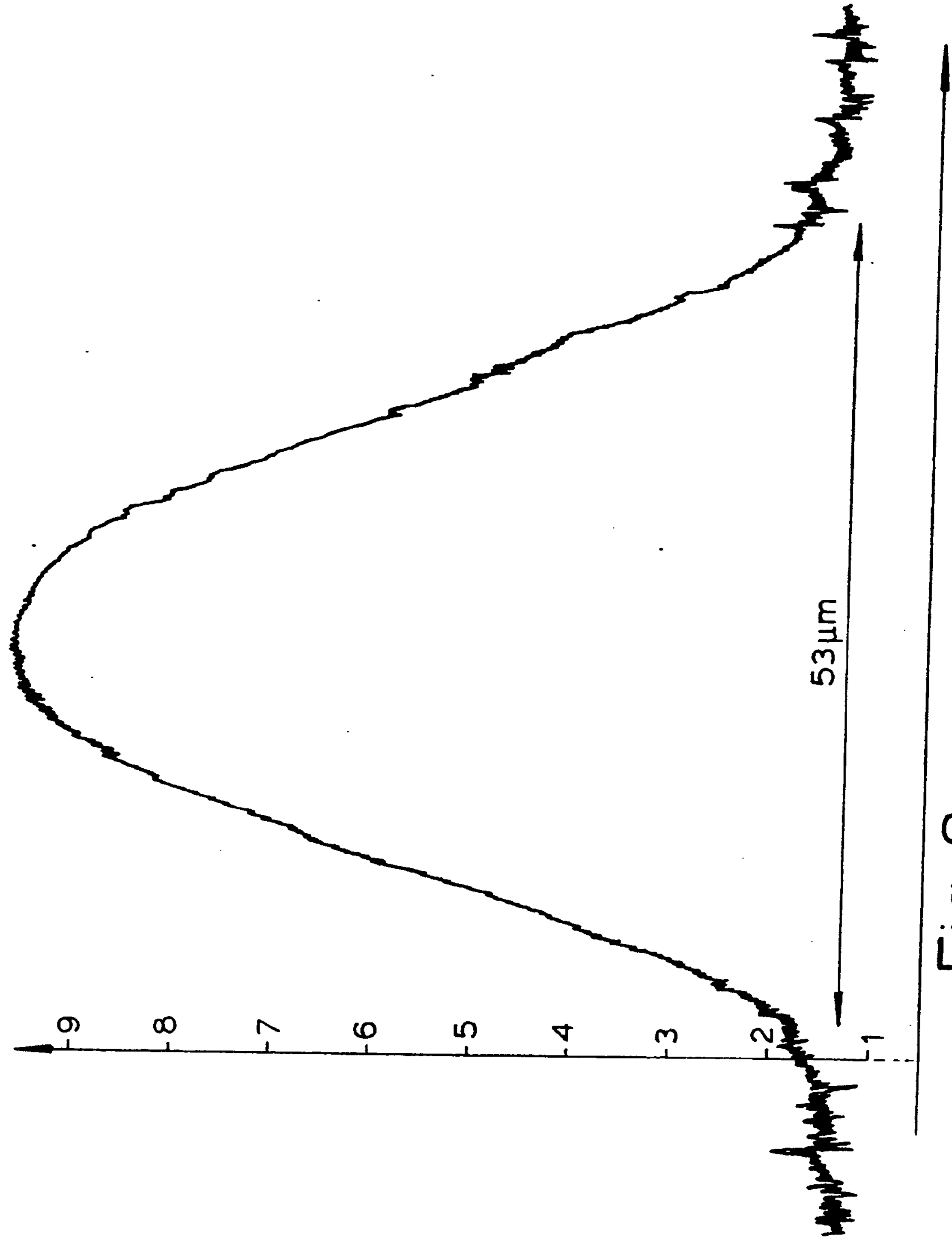

Fig. 8

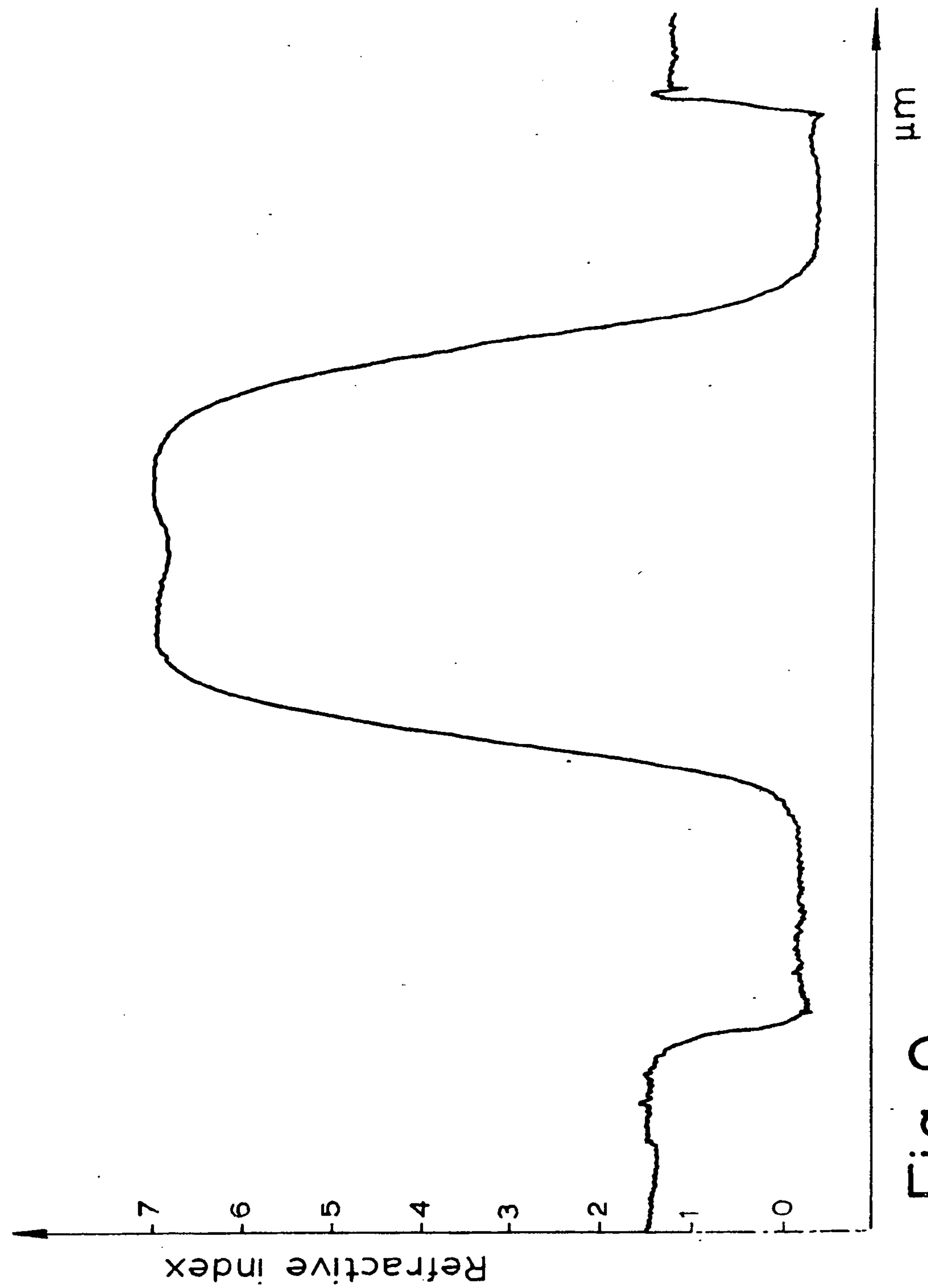

Fig. 9

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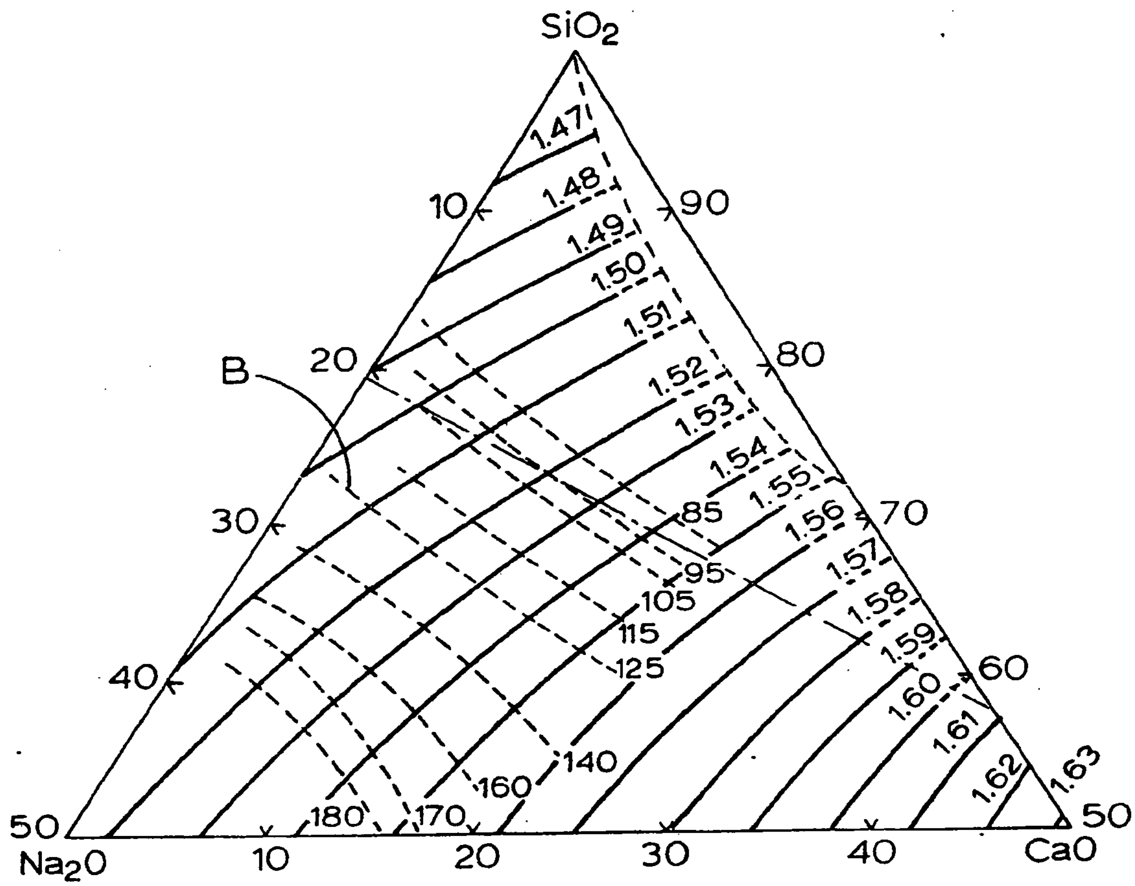

-·—·- Limit of immiscibility region.

——— Lines of equal refractive index.

----- Lines of equal thermal expansion 25-400°C x 10^7

Fig.10

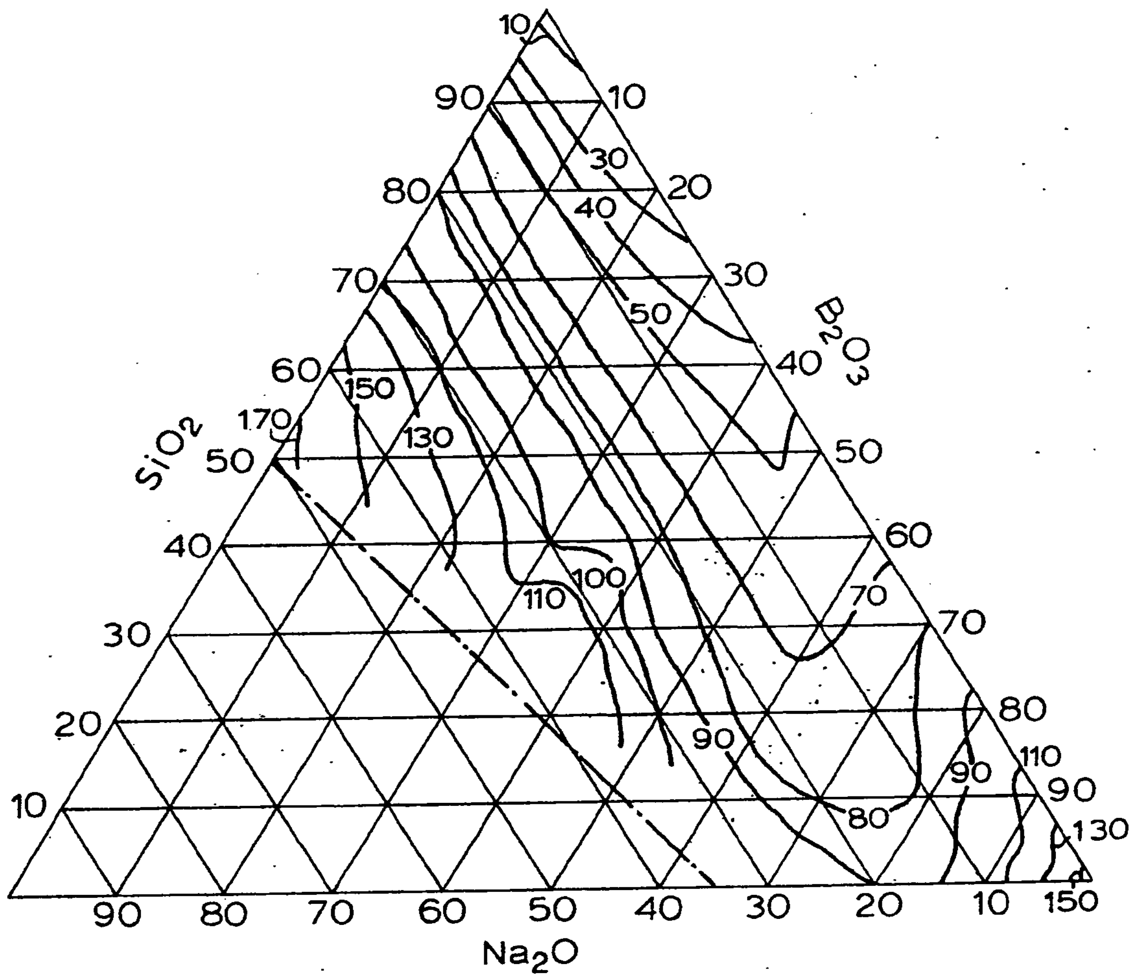
SiO2
B2O3
Na2O
10
90
80
70
60
50
40
30
20
10
20
30
40
50
60
70
80
90
150
170
130
110
100

Fig. 11

SPECIFICATION

Improvements in or relating to optical fibres and glasses

The present invention relates to optical fibres and to glasses suitable for the manufacture of optical fibres. The invention is especially concerned with graded index optical fibres and their production by thermal diffusion using the double crucible drawing technique.

In order to produce optical fibres suitable for use in telecommunications systems it is necessary to ensure that the loss in the optical fibres is 20dB/km or less. This requirement imposes stringent conditions on the quality of the glasses from which the fibres are made. For example, it is important that such glasses should have a low concentration of transition metal ions and water, which give rise to absorption bands. It is also important that phase separation and devitrification should not occur in the glasses when the fibre is drawn, because even if present to only a slight extent these effects will result in glasses with a high scatter loss.

Up to the present time greatest success has been encountered with pure and doped vitreous silicas. It is possible to produce vitreous silica in an extremely pure state, so that absorption losses due to impurities are as low as 2dB/km. In order to produce a second glass, with a refractive index different from that of pure silica, small quantities of dopants, for example, titanium dioxide, are added. In this way optical fibres can be made with a doped silica core and a pure silica cladding. Such optical fibres have an extremely low loss. Because, however, of the higher softening point of vitreous silica, there are difficulties in the preparation of optical fibres from these materials. For example, the usual technique used in the fabrication of dielectric optical waveguides is to prepare a preform consisting of a clad rod and then to draw this down to a suitable diameter to form the dielectric optical waveguide.

From the point of view of convenience of manufacture the double crucible technique for drawing fibres is ideal. This technique involves melting two glasses, one in a first crucible and the other in a second crucible, the first crucible being located within the second crucible. Both crucibles have drawing nozzles. The fibre thus formed is a clad fibre which is capable of acting as a dielectric optical waveguide. Ideally low melting point glasses are required for the double crucible technique. Such glasses are however complex, containing as a rule at least three oxides, and this introduces problems in keeping the glass losses at a sufficiently low level to permit the production of satisfactory optical fibres. US Patent Specification No 3 957 342 describes and claims a family of sodium borosilicate glasses of low softening point and low absorption and scatter loss which has proved highly satisfactory for the production of stepped index optical fibres.

The double crucible drawing technique is especially well adapted for the production of graded index fibre by thermal diffusion: see, for example, US Patent Specification No. 4 040 807 and Proceedings of the Second European Conference on Optical Fibre Communications, Paris, September 1976, pages 21–26. In this process, the core and clad glasses are subjected to a heat treatment which permits inter-diffusion of the mobile oxides in the two glasses, this heat treatment being carried out during the drawing operation by controlling the length of the drawing nozzle in the double crucible. Using the glasses described and claimed in US Patent Specification No. 3 957 342, graded index fibre suitable for a wide range of applications can be produced by this process, but the quality is not of the very highest.

The present invention is concerned with a family of glasses related to those defined in US Patent Specification No. 3 957 342, but modified by the addition of alkaline earth metal oxides. These glasses shown considerable potential for the production of high quality graded index fibre by the double crucible method. It is believed that the oxide responsible for the gradation of refractive index is the alkaline earth metal oxide. Glas[illegible] for fibre core and cladding may readily [illegible]duced, the two glasses having significantly [illegible]nt refractive indices. If desired, the glasses may be matched so as to have substantially the same coefficient of thermal expansion, but this is not essential.

Previously it had been thought that calcium oxide, for example, was not able to diffuse readily at fibre-drawing temperatures. We have, however, demonstrated that this is incorrect, and that calcium oxide and other alkaline earth metal oxides can be used in thermal diffusion techniques for the production of graded index fibre. This represents a major advance in the state of the art with regard to the production of graded index fibre using the double crucible technique.

According to a first aspect of the present invention there is provided a four-component glass suitable for the manufacture of optical fibre, the said glass having a composition calculated by taking a particular notional sodium oxide-boric oxide-silica composition lying within the range defined by region A of Fig. 1 of the accompanying drawings, and partially replacing sodium oxide or sodium oxide and silica by one or more alkaline earth metal oxides in such a proportion that the total content of alkaline earth metal oxide in the glass is within the range of from 0 to 20 mole per cent, the composition of the glass lying outside the region of compositions that undergo phase separation or devitrification during optical fibre production.

The glass of the invention preferably contains only one alkaline earth metal oxide, and that oxide is preferably calcium oxide or barium oxide.

It appears that any soda-boro-silicate glass falling within the region A of Fig. 1 of the accompanying drawings can be modified by the addition of an alkaline earth metal oxide to form a glass suitable for use in the production of optical fibre. The upper limit for silica has been set at about 70 mole per cent because above this limit difficulties in homogenisation and in melting in silica crucibles are encountered. The lower limit for silica has been set at about 50 mole per cent because of poor glass durability

below this value. The lower limit for sodium oxide has been set at 13 mole per cent because of problems due to phase separation of the glass below this limit and the upper limit has been set at 33 mole per cent because of lack of data on glasses with higher soda content.

A glass according to the invention may advantageously be paired with a glass having the corresponding unsubstituted soda-boro-silicate composition to make optical fibre, the glass of the present invention being used for the core and the unsubstituted glass for the cladding. Advantageously, the thermal expansivities of the two glasses may be matched, ie, the proportion of alkaline earth metal oxide in the core glass may be such that the thermal expansion coefficient between 0°C and the glass transition temperature of the four-component glass is substantially the same as that of the corresponding soda-boro-silicate glass.

If the alkaline earth metal oxide is calcium oxide, thermal expansivity matching may be achieved if substitution of sodium oxide and silica by calcium oxide is in such a proportion that the total molar percentage (Na_2O + $XCaO$) in the four-component glass is equal to the molar percentage of Na_2O in the three-component glass, where $X = 0.34 \pm 0.03$. The basis of this relationship is given in detail in Example 1 below.

According to a second aspect of the present invention there is provided a glass optical fibre having a core and a cladding, the core comprising a first glass, according to the invention, as previously defined, and the cladding comprising a second glass of different refractive index from the first glass and having a soda-boro-silicate composition lying within the range defined by region A of Fig. 1 of the accompanying drawings.

As indicated above, the composition of the cladding glass is advantageously also the notional composition from which the four-component composition of the core glass is derived by substitution. This is not, however, essential.

The thermal expansion coefficients of the core and clad glasses are advantageously substantially equal.

Preferably the said optical fibre is a graded index fibre and the gradation of refractive index is produced by thermal diffusion.

According to a third aspect of the present invention there is provided a glass optical fibre having a core and a cladding both made of glasses according to the invention as previously defined, the refractive indices of the core and cladding glasses being different from one another.

Preferably the said optical fibre is a graded index fibre and the gradation of refractive index is produced by thermal diffusion. Advantageously the core and clad glasses contain different alkaline earth metal oxides, the oxide of the heavier metal normally being in the core glass. For example, the core glass may contain barium oxide and the cladding glass calcium oxide, or the core glass may contain calcium oxide and the cladding glass magnesium oxide.

According to a fourth aspect of the present invention there is provided a graded index glass optical fibre having a core of a glass comprising

(a) silica,

(b) boric oxide,

(c) one or more alkali metal oxides selected from sodium oxide and potassium oxide, and

(d) one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide,

and a cladding of a glass comprising

(a) silica,

(b) boric oxide,

(c) one or more alkali metal oxides selected from sodium oxide and potassium oxide,

and optionally,

(d) one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide, barium oxide and magnesium oxide,

the said core and said cladding glasses having different refractive indices and having compositions selected to exclude glasses which undergo phase separation or devitrification during fibre production, the said gradation of refractive index being at least partly caused by a composition gradient of one or more alkaline earth metal oxides.

If desired, the thermal expansion coefficients of the core and clad glasses may be matched.

Calcium oxide, barium oxide and strontium oxide all behave similarly in glasses and all of these oxides are suitable additives for the core glass of the fibre according to the invention. The dependence of refractive index on alkaline earth metal oxide content is much stronger for barium oxide than for calcium oxide, so that a given molar percentage of barium oxide should give a fibre of higher numerical aperture than could be produced using the same amount of calcium oxide. Magnesium oxide lowers the refractive index slightly and is therefore useful as an additive to cladding glasses. Possible combinations of alkaline earth metal oxides giving the correct refractive index relationships include the following:

Core	*Cladding*
CaO	—
SrO	—
BaO	—
CaO	MgO
SrO	MgO
BaO	MgO
SrO	CaO
BaO	CaO
BaO	SrO

Furthermore, the alkali metal oxide present in the core and cladding glasses may be either sodium oxide or potassium oxide, giving a further area of choice. The potash-boro-silicate glass system is in many ways similar to the soda-boro-silicate system except that the region of stable glass formation is smaller. If, for example, sodium oxide is used in the core glass and potassium oxide in the clad glass, sodium-potassium exchange can occur in the double crucible in addition to alkaline earth metal oxide diffusion. The provision of several diffusion species

enables a better approach to the optimum refractive index profile to be produced.

One glass pair which has been tested and found to be promising (see Example 5 below) is one in which the core glass contains barium oxide, sodium oxide, silica and boric oxide and the cladding glass contains calcium oxide, potassium oxide, silica and boric oxide. During fibre production sodium-potassium exchange occurs with a fast diffusion coefficient and barium oxide-calcium oxide exchange occurs with a slower diffusion coefficient, the diffusion taking place with little change to the glass network.

Other oxides may be added to the glasses according to the invention, up to a total of about 5 mole per cent, the only limitation on these additives being that they should not cause substantial worsening of the optical properties, for example, absorption loss of the glass. For example, arsenic trioxide may be added, as described in US Patent Specification No 3 957 342, to stabilise the redox state of the glass, or alumina may be added to improve the chemical durability. The use of the latter additive may be advantageous in the case of glasses containing potassium oxide.

The following Examples illustrate the invention. The batch materials used for the preparation of the various glasses described were commercially available materials. The boric oxide, sodium carbonate, potassium carbonate, alumina and silica used in Examples 1 to 4 typically contained from 0.05 to 0.2 ppm by weight of iron, 0.01 to 0.04 ppm by weight of copper, less than 0.05 ppm by weight of chromium and less than 0.01 ppm of other transition elements. The ultra-pure calcium carbonate and barium carbonate used contained less than 100 parts by weight in 10^9 of manganese, less than 20 parts by weight in 10^9 of iron, less than 10 parts by weight in 10^9 of copper, less than 10 parts by weight in 10^9 of nickel, less than 30 parts by weight in 10^9 of chromium and less than 5 parts by weight in 10^9 of cobalt. Less pure materials were used in Examples 5 and 6.

In the Examples reference will be made to the accompanying drawings, in which:

Figure 1 shows a triaxis plot of the soda-boro-silicate glass system,

Figure 2 shows the refractive index profile of the optical fibre of the invention described in Example 1,

Figure 3 shows a plot of total insertion loss against wavelength for the fibre of Example 1,

Figure 4 shows the pulsewidth response for the fibre of Example 1,

Figure 5 shows the refractive index profile of the fibre of Example 2,

Figure 6 shows the refractive index profile of the fibre of Example 3,

Figure 7 shows the refractive index profile of the fibre of Example 4,

Figure 8 shows the refractive index profile of the fibre of Example 5,

Figure 9 shows the refractive index profile of the fibre of Example 6,

Figure 10 shows a triaxis plot of thermal expansion coefficient data for the soda-lime-silicate glass system based on published data, and

Figure 11 shows a triaxis plot of thermal expansion coefficient data for the soda-boro-silicate glass system based on published data.

COMPARATIVE EXAMPLE

Referring to Fig. 1 of the accompanying drawings, points representing two soda-boro-silicate glasses which have been used to produce graded index optical fibre by thermal diffusion with a double crucible are labelled 1 and 2, 1 being the core glass and 2 the cladding glass. Graded index fibre produced from these glasses had a total optical loss of 9–15dB/km, a part of which was of unknown origin, ie, due neither to absorption loss nor to Tayleigh scatter loss. The pulse broadening of this fibre was in the range of from 1–5ns/km. Furthermore, when viewed optically, the core displayed a ring structure of uncertain origin. Finally, the numerical aperture had a typical value of 0.12. While this fibre is of use for certain applications, it is not ideal for telecommunications purposes. The low pulse broadening is probably caused at least in part by inter-mode coupling which would account for the poor total loss. It is suspected that the visible ring may in some way be produced by thermal mismatch between the core and cladding glasses. The diffusing species producing the graded index in this glass pair is of course sodium oxide. Using soda-boro-silicate glasses the problem of obtaining a thermal expansion match between core and cladding and at the same time getting a reasonably large numerical aperture by obtaining a significant difference between core and cladding refractive indices is extremely difficult to solve. For this reason it was decided to look into the possibility of modifying the simple soda-boro-silicates by the addition of a further oxide.

Despite the fact that calcium oxide would appear to be an unlikely material to use because it was believed to have a low diffusion coefficient, it was decided to try this material because there was a little ultra-pure calcium carbonate available in the laboratory at a time when no other ultra-pure materials apart from boric oxide, silica and sodium carbonate were available. Much to our surprise we discovered that, contrary to previously held beliefs, calcium oxide was capable of diffusing at the drawing temperature of the optical finres with a diffusion coefficient of from 10^{-8} to $10^{-7}cm^2 sec^{-1}$, only very slightly slower than that of sodium oxide. The explanation for this discovery would appear to be that previous measurements of diffusion coefficient for calcium oxide were made at or below the glass transition temperature where the diffusion coefficient of calcium oxide is at least 100 times lower than that for sodium oxide. Calcium oxide has, however, a high activation energy for diffusion. This means that the diffusion coefficient increases with temperature much more rapidly for calcium oxide than for sodium oxide, hence the high diffusion coefficient for calcium oxide at the fibre drawing temperature.

EXAMPLE 1

A core glass was produced having the following composition: sodium oxide 22.30 mole per cent, boric oxide 15.00 mole per cent, silica 54.70 mole per cent, calcium oxide 8 mole per cent. The glass was prepared by the method described in detail in US Patent Specification No 3 957 342, ie, appropriate

batch material was melted to produce molten glass, and a mixture of carbon monoxide and carbon dioxide was bubbled through the molten glass in order simultaneously to optimise the redox state of the glass and to homogenise and dry it. The glass also contained about 0.1 mole per cent of arsenic trioxide as a redox buffering oxide, as also described in US Patent Specification No 3 957 342.

The glass composition was derived from a notional soda-boro-silicate composition of sodium oxide 25.00 mole per cent, boric oxide 15.00 mole per cent and silica 60.00 mole per cent (indicated by point 3 in Fig. 1), the calcium oxide replacing both soda and silica.

A graded index fibre was drawn using the four-component glass described above for the core and, for the cladding, a soda-boro-silicate glass of the composition given insthe previous paragraph. The fibre was drawn using a Johnson Mathey platinum double crucible with a 10cm nozzle. The core diameter of the fibre was 46 microns.

The refractive index profile of the fibre is shown in Fig. 2. This is a slightly over-diffused profile, ie, too much diffusion has occurred to give the optimal parabolic refractive index distribution. The extent of diffusion Ø, which ideally should have a value of from 0.06 to 0.08, was calculated from the measured profile to have a value of 0.20. The quantity Ø is given by the equation:

$$\varnothing = \frac{Dt}{A^2} = \frac{DL}{a^2 v}$$

where D is the diffusion coefficient (dependent on temperature),
t is the residence time of the glass in the nozzle (also temperature-dependent),
A is the radius of the core stream in the double crucible,
L is the length of the diffusion nozzle of the double crucible,
a is the radius of the fibre, and
v is the pulling speed of the fibre.

It will be seen that the extent of diffusion can be reduced without much difficulty, by, for example, reducing the length of the nozzle, increasing the pulling speed or decreasing the core size. Increasing the amount of diffusion is much more difficult.

Fig. 3 shows a plot of total loss against wavelength for full numerical aperture launch. From this Figure it can be seen that the total insertion loss of the fibre at 850 to 900 nanometres is 8.2dB/km. The absorption loss at selected wavelengths is indicated on Fig. 3 by a series of crosses, showing the scatter loss to be approximately 2.5dB/km which approaches the theoretically predicted loss due to Rayleigh scattering. This means that pulse width measurements on this fibre will give meaningful results. The pulse width of a one-nanosecond pulse after transmission through 1.91km of fibre is shown in Fig. 4. From this it can be shown that the pulse broadening fro the fibre is 2.8ns/km.

The numerical aperture was calculated from the refractive index profile to be 0.18. As will be seen below (Examples 5 and 6) the use of barium oxide instead of calcium oxide in the core glass gives higher numerical aperture values; the use of a higher proportion of calcium oxide has a similar but less marked effect.

From the various figures quoted above it will be apparent that this glass pair is an extremely good combination to use for high-bandwidth low-loss graded index fibre. Successive lengths of fibre drawn from this glass pair gave completely reproducible properties, as did fibre from different fibre patches. It will be noted that the composition of the core glass was computed from the clad glass composition in accordance with the equation

$$(Na_2O + 0.34CaO)_{core} = (Na_2O)_{clad}$$

mentioned above, ie, the thermal expansivities of the core and clad glasses are matched. The matching was tested by mleting samples of the two glasses, one on top of the other, in a crucible, and then cooling annealing and sectioning the resulting composite. The sample obtained was free from cracks and exhibited only minor stress at the interface when examined in a strain viewer. This indicates that both glasses had substantially the same thermal expansion coefficient.

The matching occurs because the substituion of calcium oxide for sodium oxide and silica has been carried out in such a manner that glass compositions with increasing calcium oxide lie on a line of constant expansion coefficient. In Fig. 10 lines of equal exapnsion coefficient for the soda-lime-silicate system are shown. In Fig. 11 lines of equal expansion coefficient for the soda-boro-silicate system are shown. Figs. 5 and 6 are based on published data originating from different sources. While the data for both Figs. 10 and 11 are reasonably internally consistent, there is disagreement between the absolute values. To overcome this problem, it has been assumed that, in the region of interest, the expansivity of soda-boro-silicate glasses is independent of the ratio of boric oxide to silica; this can be clearly seen from Fig. 11. Turning to Fig. 10, in terms of expansivity boric oxide and silica can be regarded as the same material so that only the variation of expansivity with sodium oxide and calcium oxide need be considered. The equation of a line of constant expansivity in the soda-line-silicate system is therefore determined. For the line marked "B" in Fig. 10 the equation is

$$Na_2 + 0.34CaO = Na_2O$$

content of the binary soda-silicate glass having a given thermal expansion coefficient. By varying sodium oxide and calcium oxide in accordance with this equation glasses having the same thermal expansion coefficient will be produced. The coefficient of 0.34 appearing in the above equation should not vary appreciably with varying glass compositions in the region A of Fig. 1, since when these are transposed to Fig. 10, the lines of constant expansion coefficient are all substantially parallel.

EXAMPLE 2

A fibre was prepared from a core glass having a composition as described in Example 1 and a cladding glass having the composition sodium oxide 25.00 mole per cent, boric oxide 12.50 mole per cent

and silica 62.50 mole per cent. The clad composition is represented by point 4 on Fig. 1. The glass was prepared as described in Example 1 and the fibre was again drawn using a Johnson Mathey platinum double crucible with a 10cm nozzle; the core diameter was 53 microns.

The refractive index profile is shown in Figure 5. The extent of diffusion ϕ was calculated to be 0.05, ie, the fibre is slightly under-diffused.

The best loss value on this fibre was found to be 6.5dB/km at 850nm, and the pulse broadening was about 2ns/km. The maximum numerical aperture was 0.197.

This glass pair is clearly suitable for use in the production of high-bandwidth low-loss graded index fibre. Use of barium oxide instead of calcium oxide in the core should result in a higher numerical aperture.

EXAMPLE 3

Graded-index fibre was produced from a core glass having the composition sodium oxide 17.30 mole per cent, boric oxide 17.50 mole per cent, calcium oxide 8.00 mole per cent, silica 57.20 mole per cent and a clad glass having the composition sodium oxide 20.00 mole per cent, boric oxide 17.50 mole per cent and silica 62.50 mole per cent. The glasses were prepared as described in Example 1. The clad composition is represented by point 5 on Fig. 1, and the core composition is derived from that composition by substitution of calcium oxide, to an extent of 8.00 mole per cent, for soda and silica.

The fibre was drawn using a Johnson Mathey platinum double crucible with a 10cm nozzle. The core diameter of the fibre was 46 microns. Its refractive index profile is shown in Fig. 6; this is a slightly under-diffused profile, the Ø-value being approximately 0.04. The best loss value obtained with this fibre was 6.4dB/km at 850nm.

EXAMPLE 4

A soda-boro-silicate glass having the composition sodium oxide 22.50 mole per cent, boric oxide 17.50 mole per cent and silica 60.00 mole per cent (point 6 on Fig 1) was chosen as a suitable cladding glass for graded-index fibre and this time a core composition was selected by replacing soda only, not soda and silica, by calcium oxide. The core composition was sodium oxide 15.00 mole per cent, boric oxide 17.50 mole per cent, calcium oxide 7.50 mole per cent and silica 60.00 mole per cent. Both glasses were prepared as described in Example 1.

Fibre was drawn from this glass pair using a Johnson Mathey platinum double crucible with a 10cm nozzle. The core diameter was 40 microns. The refractive index profile is shown in Fig. 7; the Ø-value was calculated to be 0.06, which is at the lower end of the ideal range. The maximum numerical aperture was 0.150, and the best loss value was 9.0dB/km at 850nm.

It will be seen that this glass pair is exceptionally suitable for the production of low-loss graded-index optical fibre.

EXAMPLE 5

A core glass having the following composition was prepared: sodium oxide 19.27 mole per cent boric oxide 7.23 mole per cent, barium oxide 12.04 mole per cent, alumina 3.62 mole per cent, silica 57.82 mole per cent. The clad glass chosen had the following composition: potassium oxide 19.27 mole per cent, boric oxide 7.23 mole per cent, calcium oxide 12.04 mole per cent, alumina 3.62 mole per cent, silica 57.82 mole per cent. It will be noted that the percentages of silica and of boric oxide are the same in core and cladding, and the molar percentages of the monovalent diffusing species (Na^+ and K^+) and of the divalent diffusing species (Ba^{2+} and Ca^{2+}) are matched. The alumina was included to improve the chemical durability of the glass. The starting materials used in this Example were not of such high purity as in the previous Examples, and the gas-bubbling stage was omitted. Because of this it was not possible to obtain loss and pulse-broadening measurements on the fibre produced in this run, which was carried out purely in order to obtain a refractive index profile.

Fibre having a core diameter of 55 microns was drawn using a Johnson Mathey platinum double crucible with a 10cm nozzle. The refractive index profile is shown in Fig. 8. The Ø-value was 0.08, the best yet obtained with this class of glasses, and the maximum numerical aperture was 0.21. It will be seen that this glass pair is extremely promising for use in the production of graded-index fibre.

EXAMPLE 6

This Example illustrates the use of barium oxide in the core and calcium oxide in the clad, all other components of the two glasses being the same. As in Example 5, the starting materials were not sufficiently pure for loss and pulse-broadening measurements to be carried out.

The core composition was sodium oxide 20.00 mole per cent, boric oxide 10.00 mole per cent, barium oxide 10.00 mole per cent and silica 60.00 mole per cent, and the clad composition was identical except that 10.00 mole per cent of calcium oxide replaced the 10.00 mole per cent of barium oxide. Fibre having a core diameter of 80 microns was drawn in an Engelhard platinum double crucible with 10cm nozzle.

The refractive index profile is shown in Fig. 9. The Ø-value was calculated to be about 0.02, ie, the fibre was considerably under-diffused. This is believed to be largely atrributable to the fact that it was made in a crucible designed for large-core slightly-graded fibre; use of the Johnson Mathey crucible used in Examples 1 to 5 would be expected, on the basis of previous experiments, to increase significantly the extent of diffusion. The maximum numerical aperture of the fibre was 0.210.

CLAIMS

1. A four-component glass suitable for the manufacture of optical fibre, the said glass having a composition calculated by taking a particular notional sodium oxide-boric oxide-silica composition lying within the range defined by region A of Fig 1 of the accompanying drawings, and partially replacing sodium oxide or sodium oxide and silica by one or more alkaline earth metal oxide in such a proportion that the total content of alkaline earth metal oxide in the glass is within the range of from 0

to 20 mole per cent, the composition of the glass lying outside the region of compositions that undergo phase separation or devitrification during optical fibre production.

2. A glass as claimed in claim 1, wherein the replacement of sodium oxide or of sodium oxide and silica is such that the thermal expansion co-efficient between 0°C and the glass transition temperature of the glass is substantially the same as that of the corresponding notional sodium oxide-boric oxide-silica glass.

3. A glass as claimed in claim 1 or claim 2, wherein the alkaline earth metal oxide is barium oxide.

4. A glass as claimed in claim 1 or claim 2, wherein the alkaline earth metal oxide is calcium oxide.

5. A glass as claimed in claim 4, wherein sodium oxide and silica are so replaced by calcium oxide that the molar percentage of (Na_2O + XCaO) in the said glass is equal to the molar percentage of Na_2O in the corresponding notional sodium oxide-boric oxide-silica composition, where
$X = 0.34 \pm 0.03$.

6. A glass as claimed in claim 1, substantially as hereinbefore described in any one of Examples 1 to 4.

7. An optical fibre having a core and a cladding, the core comprising a first glass which is as claimed in any one of claims 1 to 6 and the cladding comprising a second glass of different refractive index from the first glass and having a sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Fig 1, the compositions of the first and second glasses being selected to exclude compositions which undergo phase separation or devitrification during optical fibre production.

8. An optical fibre as claimed in claim 7, wherein the notional sodium oxide-boric oxide-silica composition from which the composition of the first glass is derived is the composition of the second glass.

9. An optical fibre as claimed in claim 7, substantially as hereinbefore described in any one of Examples 1 to 4.

10. An optical fibre having a core and a cladding each comprising a glass as claimed in any one of claims 1 to 6, the refractive indices of the core and cladding glasses being different from one another.

11. An optical fibre as claimed in claim 10, wherein the core glass contains the oxide of a first alkaline earth metal and the cladding glass contains the oxide of a second alkaline earth metal, the atomic number of the said first alkaline earth metal being greater than the atomic number of the said second alkaline earth metal.

12. An optical fibre as claimed in claim 11, wherein the first alkaline earth metal is barium and the second alkaline earth metal is calcium.

13. An optical fibre as claimed in claim 11, wherein the first alkaline earth metal is calcium and the second alkaline earth metal is magnesium.

14. An optical fibre as claimed in any one of claims 10 to 13, wherein the compositions of the core and cladding glasses are based on the same notional sodium oxide-boric oxide-silica composition.

15. An optical fibre as claimed in any one of claims 10 to 14, which is graded index fibre in which the gradation of the refractive index is produced by thermal diffusion.

16. An optical fibre as claimed in claim 10, substantially as hereinbefore described in any one of Examples 1 to 6.

17. A graded index glass optical fibre having a core and a cladding, the core glass comprising

a. silica,

b. boric oxide,

c. one or more alkaline metal oxides selected from sodium oxide and potassium oxide, and

d. one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide, and the clad glass comprising

a. silica,

b. boric oxide,

c. one or more alkaline metal oxides selected from sodium oxide and potassium oxide, and, optionally,

d. one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide, barium oxide and magnesium oxide,

the core and cladding glasses having different refractive indices and having compositions selected to exclude compositions which undergo phase separation or devitrification during optical fibre production, and the said gradation of refractive index being at least partly caused by a composition gradient of one or more alkaline earth metal oxides.

18. An optical fibre as claimed in claim 17, wherein components (d) of the core glass comprises calcium oxide and the cladding glass contains no component (d).

19. An optical fibre as claimed in claim 17, wherein component (d) of the core glass comprises barium oxide and the cladding glass contains no component (d).

20. An optical fibre as claimed in claim 17, wherein component (d) of the core glass comprises the oxide of a first alkaline earth metal and component (d) of the cladding glass comprises the oxide of a second alkaline earth metal, the atomic number of the said first alkaline earth metal being greater than that of the said second alkaline earth metal.

21. An optical fibre as claimed in claim 20, wherein component (d) of the core glass is barium oxide and component (d) of the cladding glass comprises calcium oxide.

22. An optical fibre as claimed in claim 20, wherein component (d) of the core glass is calcium oxide and component (d) of the cladding glass is magnesium oxide.

23. An optical fibre as claimed in any one of claims 17 to 22, wherein components (c) of the core and cladding glasses both comprise sodium oxide.

24. An optical fibre as claimed in any one of claims 17 to 22, wherein component (c) of the core glass comprises sodium oxide and component (c) of the cladding glass comprises potassium oxide.

25. An optical fibre as claimed in any one of claims 17 to 24, wherein the core and cladding glasses each contain from 50 to 70 mole per cent of component (a), and from 13 to 33 mole per cent of com-

ponent (c).

26. An optical fibre as claimed in claim 17, substantially as hereinbefore described in any one of Examples 1 to 6.

27. An optical communications system including one or more optical fibres as claimed in any one of claims 7 to 26.

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